

# PATENT SPECIFICATION

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## (54) SPECTROGRAPHIC STANDARDS

- (71) We, CONTINENTAL OIL COMPANY, a Corporation organised under the laws of the State of Delaware, United States of America, of 1000 South Pine Street, Ponca City, Kay County, State of Oklahoma, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to spectrographic analysis, and more particularly to standards for calibration of spectrographic analysis equipment.
- For many years it has been known that the metal elements of the periodic table, when vaporized, e.g., by burning, emit characteristic wave lengths and, when solutions of such elements are exposed to X rays and the rays analyzed, characteristic wave lengths are obtained. By measuring these characteristic waves, shown as lines on a screen or film, unknown materials can be analyzed quantitatively. More recently, it has been found that, by measuring the intensity of a predominating light wave and comparing this with a known standard, a quantitative determination can be made. There are a number of different types of such analytical spectrographic equipment, including flame spectrography, atomic adsorption spectrography and X-ray emission spectrography. Characteristic of such equipment is the use of a shield having slits at predetermined positions to pass predominant rays and means for measuring the intensity of the rays passing these slits, such measurements generally being referred to as counts. Those skilled in the art will recognize that the above description is oversimplified, as such workers in the art are well acquainted with the operation and theory of such spectrographic analysis.
- It is also known by those skilled in the art of spectrographic analysis that the equipment must be calibrated from time to time using known standards, that is, aliquots of a known hydrocarbon soluble sample are diluted to known values and two or more values measured and plotted. The unknown is then measured or counted, and the percent of the unknown is determined from the standard curve. As was previously stated, the quantitative analysis equipment ordinarily provides for a screen of the light defraction with slits to pass a predominant wave length for the various elements or metals. When a sample being analyzed comprises several such elements, minor waves from some of the elements can cause the equipment to give a false count for the element being determined. Therefore, it is desirable that the standard contain the elements in approximately the same concentration as the unknown. This can be readily accomplished by taking a first approximation and adjusting the standard. Unfortunately, the standards now available, usually naphthenates of cationic and amphoteric metals, various esters, and soluble salts or acids of the anionic metals, are not always compatible. That is, they either are not mutually soluble in the same solvent or they react and form precipitates. It is also well known that the presently available commercial standards have relatively short shelf life.
- Such spectrographic analyses are useful for analyses for the various metals generally. Examples of such uses include biomedical analyses, such as blood, tissue, and urine analyses, resin analyses to determine level of certain metal or organometal stabilizers, fillers and the like, and in fact, almost any analysis wherein the percent metal in an unknown is desired. Recently, it has been found that analysis of crankcase oil is a valuable tool for determining abnormal wear in an internal combustion engine. That is, as the engine operates, there is a normal wear, and a spectrographic analysis for the metals used in the engine components will reveal the extent of wear. In case of a failure, say of a bearing, the metal content will be excessively high and the necessary steps can be taken to correct the condition prior to a complete engine failure. While such information reduces maintenance costs, generally,

[Price 25p]

and in the case of aircraft, such routine analysis becomes essential. For example, during the Military-Industry Spectrometric Oil Analyses Symposium sponsored by the Directorate of Air Force Aerospace Fuels, San Antonio Air Material Area, Kelly Air Force Base, Texas, held July 18, 19, and 20, 1967, it was estimated by 1970 the airforce alone will be analyzing 443,000 samples a month for wear components and will be operating 180 on-base analyzers. It was also the consensus of the speakers of the Symposium that the current available standards leave something to be desired.

According to the present invention there is provided a method of spectrographic analysis of metals wherein the intensity of a beam of light passed through an unknown solution containing said metals is compared to the intensity of a beam of light passed through a comparative standard containing said metals, the improvement comprising utilizing as the comparative standard a material consisting of oil-soluble metal hydrocarbon sulfonates or dispersions of metals in such oil-soluble sulfonates. Such standards have indefinite shelf life and any combination of metals can be combined without precipitation.

A number of patents have issued for the preparation of oil-soluble metal sulfonates and metal dispersions in such oil-soluble sulfonates. Typical of such patents are U.S. 3,277,002 to Mack W. Hunt et al and 3,250,710 to Mack W. Hunt. The primary interest in such materials has been in the preparation of overbased sulfonate compositions for use in corrosion inhibitor lubricants. While most of these patents are directed to overbased materials, the methods are applicable to the preparation of the neutral oil-soluble metal organo-sulfonate. In our invention, either overbased or neutral materials are operable, however, we do prefer that the metal-organo sulfonate be neutral or only slightly overbased.

With cationic and amphoteric metals, e.g., those which will react with acid to form a salt, neutral sulfonates can be prepared which are simply the metal salt of the oil-soluble organic sulfonic acid. With the anionic metals, an overbased sulfonate is first formed and the acid or oxide of the metal is added to react with the excess base, as more fully described hereinafter and as has been previously disclosed in such patents previously referred to.

Suitable oil-soluble hydrocarbon sulfonic acids include alkane sulfonic acid, aromatic sulfonic acid, alkaryl sulfonic acid, aralkyl sulfonic acid, and the natural petroleum mahogany sulfonic acids. The mahogany sulfonic acids include any of those materials which may be obtained by concentrated or fuming sulfuric acid treatment of petroleum fractions, particularly the higher boiling

lubricating oil distillates and white oil distillates. The higher molecular weight petroleum oil-soluble mahogany sulfonic acids are condensed-ring compounds, which condensed-rings may be aromatic or hydroaromatic in nature. Alkyl and/or cycloalkyl substituents may be present in the mahogany sulfonic acids.

Illustrative of one class of suitable hydrocarbons nuclei are the materials made by reaction of a benzene hydrocarbon with a "wax hydrocarbon." Wax hydrocarbons are derived from paraffin wax having an average carbon atom content of 18 to 24, or even more. Normally, two of the wax hydrocarbon side-chains are present in the final product and these compounds are spoken of as diwax-benzenes.

The term "aromatic hydrocarbon" is intended to include those hydrocarbons containing a benzene-ring or a number of condensed benzene-rings, for example, benzene, naphthalene and anthracene. Alkyl and/or cycloalkyl sidechains may be present. The term "benzene hydrocarbon" is intended to include all operative hydrocarbons containing a single benzene-ring and includes benzene itself. Particularly preferred members of this class are benzene, toluene, ethylbenzene and the xylenes.

An especially suitable hydrocarbon nucleus is afforded by the reaction product of a highly branched olefin with an aromatic hydrocarbon, in general, and a benzene hydrocarbon in particular, the products being alkylaromatic or alkylbenzene, respectively. These highly branched olefins are available from the petroleum industry through polymerization of propylene and/or butylene. In the case of the low molecular weight butylene polymers, the polymer normally contains 2 to 6 units. In the case of the low molecular weight propylene polymers, the polymer normally contains 2 to 8 units.

The especially preferred alkylaromatic hydrocarbons are normally prepared by reacting the olefin with the aromatic hydrocarbon in the presence of a Friedel-Crafts type catalyst, usually aluminum chloride.

The most preferred hydrocarbon nucleus for preparation of the sulfonic acid used in the process of the invention is obtained from the reaction product of propylene tetramer with benzene, using aluminum chloride catalyst. The reaction product contains a very wide range of alkylbenzenes, both in number of alkyl groups present and in the number of carbon atoms present in each alkyl group. A particular fraction of the reaction product is the most preferred hydrocarbon nucleus for the subsequent sulfonation reaction. This preferred alkylbenzene nucleus is given the name "postdodecylbenzene" and includes as the alkylbenzene components,

monododecylbenzene and didodecylbenzene in the approximate molar ratio of 2:3.

Typical characteristics of postdodecylbenzene are:

5	Specific gravity at 38°C	0.8649
	Average molecular weight	385
	Percent sulfonatable	88
	ASTM (D-158 Engler), °C:	
	I.B.P.	342
10	5%	361
	50%	379
	90%	404
	95%	413
	F.B.P.	415
15	Refractive index at 23°C	1.4900
	Viscosity at:	
	-10°C, centipoises	2800
	20°C, centipoises	280
	40°C, centipoises	78
20	80°C, centipoises	18
	Aniline point, °C	69
	Pour point, °C	-32

It is to be understood that the hydrocarbon nucleus of the sulfonic acid used in the process of the invention may be any hydrocarbon which permits the product of an overbased oil-soluble sulfonate. It is preferred to utilize alkylaromatic hydrocarbons as the nucleus.

Especially preferred are the alkylbenzene hydrocarbons having 6—24 carbon atoms in at least one alkyl group. The lower molecular weight benzene hydrocarbons as defined earlier are preferred for the benzene portion of the alkylbenzene hydrocarbon. As was pointed out above, especially suitable sulfonic acid is produced from postdodecylbenzene.

The corresponding hydrocarbon sulfonic acid is usually prepared by treating the hydrocarbon with concentrated sulfuric acid, fuming sulfuric acid or sulfur trioxide. The sulfonation of hydrocarbons is well known and details need not be given.

The dispersing aid used in preparation of the standard employed in the method of the present invention is an aliphatic compound having at least two functional groups. These functional groups, except as hereinafter stated, may be the same type or different types. The aliphatic compound contains no functional group of a type different from the hereinafter listed functional groups. One of the functional groups is either alkoxy, (—OR); amino, (—NH<sub>2</sub>); ester, (—COOR'); formyl, (—CHO); halo, (—X); hydroxy, (—OH); or keto, (=C=O). While in most instances the aliphatic compound may include two or more groups of the same type as the only functional group, in some instances it is essential that at least two different functional groups be present. Thus, the aliphatic compound contains, in addition to at least one of the above-defined functional

groups, at least one other group which is either alkoxy, amino, formyl, hydroxy or keto.

More specifically, suitable dispersing aids may be selected from one or more of the following classes of aliphatic compounds where the only carbon-carbon linkages are single bonds and the total number of carbons in the aliphatic backbone of the compound, i.e., when carbon atoms containing substituents are present, is not more than 8: aminoalcohol such as 2-aminoethanol and 2-dimethyl aminoethanol; dialkoxyalkane where alkoxy has not more than 4 carbon atoms, such as acetal (1,1-diethoxy ethane) and 1,1-dimethoxy ethane and 2,2-diethoxy propane; haloalcohol such as 1,3-dichloro-2-propanol; haloaldehyde such as chloral hydrate (trichloroacetaldehyde); hydroxyaldehyde such as aldol; hydroxyketone such as 3-hydroxy-2-butanone; ketoaldehyde such as pyruvaldehyde; and ketoester where carboxyl has not more than 4 carbon atoms, such as ethyl acetoacetate; diketone such as 2,3-pentanedione, 2,3-butanedione and 2,4-pentanedione; glycols and ether glycols such as ethylene glycol and diethylene glycol.

The reaction with the metal may be carried out with the sulfonic acid, the metal, and the dispersing aid alone. However, it is convenient to have a diluent present in the reaction zone. Preferably, this diluent is a hydrocarbon. Where a concentrate is desired, a low boiling hydrocarbon such as hexane or naphtha may be used as diluent, followed by distillative removal of the diluent, leaving metal sulfonate product.

As has been suggested, the oil-soluble metal sulfonate, as prepared above, is applicable to cationic and amphoteric metals generally. Typical of cationic metals are lithium, sodium, potassium, rubidium, cesium, beryllium, strontium, chromium, molybdenum, manganese, iron, cobalt, nickel, copper, silver, zinc, cadmium, mercury, aluminum, tin, lead, and antimony. These metals are preferably added as the hydroxide or oxide to the oil sulfonic acid in an amount to at least neutralize the acid.

With the anionic metals, it is necessary to overbase the oil-soluble sulfonic acid. That is, in the contacting zone, the base is present in an amount in excess of that theoretically needed to form the neutral metal sulfonate. Sufficient base is used to provide excess base desired to react with the anionic acid or oxide. Preferably, the overbased metal will be an alkaline earth or alkali metal in order to provide a strong base for neutralizing with the anionic metal acid or oxide. Such anionic metals are represented by boron, silicon, phosphorus, arsenic, selenium, scandium, yttrium, lanthanum, titanium, zirconium, vanadium, and gold.

Oil-soluble metal sulfonates and dispersions

- have been prepared with all of the above metals except those anionic metals beginning with scandium and analysis checked over a period of at least 6 months for comparison with commercial standards and chemical analysis and have been found to be completely stable. Whereas, with some of the naphthenates and other commercial standards, we have noted a falling off of potency or strength in some cases in as short a period of one month. In the case of calcium and barium overbased materials, we have found them stable for at least five years, and there appears to be no tendency of any of these materials to deteriorate with time. We believe from our observations of these materials and the prior art materials that the metal sulfonates proposed as analytical standards in this invention have stability for an unlimited time. While this is a subjective observation, as obviously we have not kept a sample forever, it is believed those skilled in the art will recognize the validity of this conclusion. This is especially true, since no precautions have been taken to preserve the materials we have prepared. They have been simply set on the laboratory shelf.
- The following preparations were made and illustrate the method of preparing these analytical standards.
1. Preparation of Neutral Zinc Sulfonate  
The following was charged to a 5-liter, 3-necked flask equipped for overhead distillation and mechanical mixing:
    - 2000 grams sulphonic acid solution derived from dimer alkylate bottoms. Composition: 27% acid with an average molecular weight of 435, 10% oil, and 63% hexane
    - 200 grams 100 pale oil
    - 200 grams methyl alcohol
    - 200 grams water
    - 64 grams zinc oxide
    - 20 grams filter aid
  - The above mixture was heated to reflux for 2 hours. Then the solvents were removed by heating to 150°C and then stripped with CO<sub>2</sub> for 20 minutes. The product was filtered while hot through a precoated filter. The brown oil contained 5.1% zinc.
  - Other suitable neutralizing agents would include zinc carbonate, hydroxide and the various alcoholates.
  2. Preparation of Neutral Tin Sulfonate  
The same equipment as 1. above was used and charged with:
    - 1500 grams sulfonic acid solution. This was derived from dialkylbenzene with an average molecular weight of 400. The composition of the acid was: 50% sulfonic acid with an average molecular weight of 485, 4.1% oil, and 45.9% hexane
    - 600 grams 80 pale oil
    - 300 grams water
    - 375 grams methyl alcohol
    - 118.5 grams stannous oxide
    - 20 grams filter aid
  - The above mixture was heated to reflux with mixing. Reflux was maintained for 2 hours and then the solvents were removed by heating to 150°C and then stripping with CO<sub>2</sub> for 25 minutes. The product was filtered while hot through a precoated filter. The brown oil contained 4.8% tin.
  - Other suitable neutralizing agents are stannous hydroxide and the various alcoholates.
  3. Preparation of Neutral Copper Sulfonate  
The same equipment as 1. above was used and charged with:
    - 1500 grams sulfonic acid solution. This solution had the same analysis as the acid solution of 2. above
    - 500 grams 80 pale oil
    - 400 grams methanol
    - 100 grams water
    - 100 grams cupric carbonate (basic)—malachite
  - The same general process details were used as outlined in 2. above. The green colored oil contained 4.1% copper.
  - Other satisfactory neutralization materials include: cupric hydroxide and the various alcoholates.
  4. Preparation of Neutral Nickel Sulfonate  
1500 grams sulfonic acid solution. This solution had the same analysis as the acid solution of 2. above.
    - 600 grams 80 pale oil
    - 375 grams "methyl CELLOSOLVE" (Registered Trade Mark)
    - 300 grams water
    - 117 grams nickelous carbonate
  - The same general process details were used as outlined in 2. above. The green colored oil contained 4.5% nickel.
  - Other satisfactory neutralization materials include metal hydroxides, oxides, and the various metal alcoholates.
  - Similar preparations have been made for the sulfonates of molybdenum, iron, lead, chromium, silver, magnesium, calcium, barium, manganese, cobalt, and aluminum.
  - The following example illustrates a method of preparing an anionic standard.
  - A 5-liter, 3-necked flask was equipped with a thermometer, condenser, and mechanical stirrer. The flask was charged with:
    - 2000 grams of an overbased calcium post-dodecylbenzene sulfonate having a base number of 300
    - 1500 grams isopropyl alcohol
    - 500 grams boric acid

The mixture was stirred and heated slowly. The reaction began upon mixing, as is evidenced by CO<sub>2</sub> evolution. After heating for an hour under reflux conditions, the alcohol was removed by heating to 150°C until the solvent appeared to be removed, and then the mixture was stripped with nitrogen for 15 minutes to increase complete removal of solvent. The product weighed 2260 grams and analyzed for the boron content. The sample contained 3.82% boron.

In preparing the standards a measured volume of a suitable solvent, preferably one in which the unknown is also soluble, such as a liquid hydrocarbon, preferably a paraffin of 4 to 6 carbon atoms, for example butane, hexane, and cyclohexane; a ketone, particularly methyl ethyl ketone; or a pale oil, is placed in a vessel. Knowing the content of the standard, an aliquot of the standard or standards is added to the solvent to provide the desired concentrations. Such solutions are prepared containing varying predetermined amounts of the metals of interest. At least two levels of concentration are required, and

three or more are preferred. These known samples are then run in the equipment being standardized and counts taken and plotted. The unknown, preferably in the same solvent and containing the same metals, are run and counts compared to the standard curve. From this comparison the relative amounts of the metals in the unknown can be determined. For greater accuracy, a new curve is prepared wherein the standards are added to the solvent in the same relative ratios as was indicated by the first determination and the unknown compared to the new curve. Those skilled in the art will readily understand that this procedure is desirable to compensate for any interference with the predominant wave lengths produced by the metals not being read at that particular position.

Three blends of metal organosulfonates, e.g., metal postdodecylbenzene sulfonate in a 20 weight petroleum oil, detergent and base free, were prepared containing 16 metals. The composition of these blends are shown below.

Element	Blend No. 1 Conc. (ppm)	Blend No. 2 Conc. (ppm)	Blend No. 3 Conc. (ppm)
Copper	49	520	2
Silver	30	200	2
Tin	36	221	9
Chromium	45	3	500
Aluminum	52	14	503
Iron	61	150	22
Lead	162	21	842
Calcium	1210	7996	165
Barium	1015	8072	141
Silicon	100	45	200
Manganese	352	53	2001
Boron	100	500	10
Magnesium	1059	8030	92
Molybdenum	500	100	2000
Zinc	502	7	2009
Phosphorus	500	10	2000

These blends have been used for 6 to 8 months for standardizing emission spectrography equipment. The equipment can then be utilized for determining these elements in a crankcase oil. It will be noted that calcium, barium, and magnesium are included in the blends. This is necessary, since the oils to be analyzed are overbased materials. The unknown oil is also diluted with the 20 weight motor oil by placing a known amount of the unknown in a known amount of the solvent oil.

#### WHAT WE CLAIM IS:—

1. A method of spectrographic analysis of metals wherein the intensity of a beam of light passed through an unknown solution containing said metals is compared to the intensity of a beam of light passed through a comparative standard containing said

metals, the improvement comprising utilizing as the comparative standard a material consisting of oil-soluble metal hydrocarbon sulfonates or dispersions of metals in such oil-soluble sulfonates.

2. The method of Claim 1 wherein said oil-soluble metal hydrocarbon sulfonates are derived from alkaryl hydrocarbons wherein the alkyl substituents contain at least 18 carbon atoms.

3. The method of Claim 2 wherein the metal oil-soluble sulfonate is substantially neutral.

4. The method of Claim 3 wherein the metal oil-soluble sulfonate comprises a mixture of at least two metals.

5. The method of Claim 4 wherein the metal oil-soluble sulfonates are in a paraffin oil.

6. The method of Claim 4 wherein the

metal oil-soluble sulfonates are in a ketone.

of metals according to claim 1 substantially 10  
as herein described.

7. The method of Claim 6 wherein the  
said ketone is methyl ethyl ketone.

5 8. The method of Claim 5 wherein the  
metals being determined are in a motor oil.

9. The method of Claim 8 wherein said  
motor oil is a used crankcase oil from an  
internal combustion engine.

10. A method of Spectrographic analysis

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